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(Co)polytetramethylene-adipamide articles.

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A polymer of tetramethylene diamine and adipic acid or a copolymer thereof with other amide and/or ester forming compounds is used as material for articles destined for a device comprising a fuel engine.

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TITLE MODIFIED
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ARTICLES DESTINATED FOR DEVICES COMPRISING A FUEL ENGINE AND USE OF A
POLYAMIDE FOR SUCH ARTICLES

The invention relates to articles destined for devices which comprise a fuel engine.

Articles made of polyamide materials are commonly known in the art.

5 Such articles can however only be used to a very limited extent for applications in devices which comprise a fuel engine, i.e. in applications in which the articles are destined to be subjected to increased temperatures, to stresses and/or to environments that are generally detrimental for polyamides like fuel ingredients (such as in
10 particular methanol) and certain ion species (such as in particular combinations of zinc and chloride ions).

It has now been found surprisingly that when using certain specific polyamide polymers for said applications, the stated drawbacks are considerably reduced or even avoided.

15 The polyamides used in accordance with this invention for making articles destined for a device comprising a fuel engine are polymers of tetramethylene diamine and adipic acid or copolymers there-of with other amide and/or ester forming compounds.

The polymers can contain additives normally used with
20 polyamides, such as stabilizers, antioxidants, sliding agents, whitening agents etc. In addition to tetramethylene diamine and adipic acid, up to 20 wt % of other amide and/or ester forming compounds may have been incorporated in the polymer.

The polymers may in particular consist of polytetramethylene
25 adipamide (which is being referred to as nylon 4,6) as a homopolymer or substantially homopolymer, or of copolymers of tetramethylene-diamine and adipic acid with up to 20 wt. % of lactams such as caprolactam and lauric lactam, amino acids, other diamines such as hexamethylene diamine, other dicarboxylic acids such as succinic acid,
30 sebacic acid, isophthalic acid and terephthalic acid and/or diols such as ethyleneglycol.

The used polymers should preferably have a relative viscosity value, as measured at 20 °C on a solution in 96 % sulfuric acid containig 1 g of polyamide in 100 ml of solution, of at least 2 and most preferably between 3 and 5.

5 The use of the polyamides in accordance with the invention is specifically recommended for:

Articles which are destined to be subjected to increased temperatures or stress, and in particular articles which are destined to be subjected to stress under increased temperature; this is
10 for instance the case for machine or vehicle parts under the hood of or close to a combustion engine.

Articles which are destined to be subjected to alcohol containing environments, such as in particular methanol; this is for instance the case for articles which are liable to come in contact
15 with alcohol- in particular methanol- containing engine fuels.

Articles which are destined to be subjected to zinc and/or chloride ion environments; this is for instance the case for machine or vehicle parts which are placed in an environment where there are also galvanized (Zn) metal parts and a medium which contains chloride
20 ions (for instance sea-water; road salts etc).

The use of the polyamides according to the invention is very particularly recommended for articles which are destined to be subjected to stresses of more than 3 N/mm² under alcohol and/or zinc chloride containing environments.

25 The expression 'device which comprises a fuel engine' as used in this specification is intended to include any kind of device, either stationary, movable or self propelled which is provided with a fuel engine; such expression is in particular intended to cover fuel engine machines and devices of any kind, and fuel engine bearing or
30 propelled vehicles of any kind such as motor cars, air planes, boats etc.

The invention will be now elucidated in more detail by means of examples of specific polyamide materials, having regard to the unexpected properties thereof in respect of the scope of articles for
35 which they are destined in accordance with this invention.

Example 1

Hot water/steam and thermal stability of injection moulded polyamide test bars.

The hot water/steam stability and the thermal stability of nylon 4.6 was compared to that of nylon 6 and nylon 6.6 using the ISO R 527 standard test method.

Test bars for the tensile strength measurements were injection moulded from samples of the following (unstabilised) polyamides:

- Nylon 6: Ultramid B₃ (which is a trade mark of BASF)
 10 Nylon 6.6: Ultramid A₃ (which is a trade mark of BASF)
 Nylon 4.6: a polytetramethylene adipamide sample having a relative viscosity value 3.4.

The test bars were moulded using a standard laboratory injection moulding machine. For nylon 6 and nylon 6.6 the moulding conditions were in accordance with those set forth by the supplier.
 15 For nylon 4.6 a nozzle temperature of 310 °C and a mould temperature of 80 °C were used, and an injection pressure of 1500 atm. and an after injection pressure of 370 atm.

The ageing of the testbars was carried out in an autoclave
 20 at 120 °C under water/steam atmosphere under nitrogen pressure for the hot water/steam stability test and in an air oven at 120° for the thermal stability tests; the time after which tensile strength fell to 50 % of its initial value was determined. The results of these measurements are represented in table 1.

25 Table 1

	Hot water/steam stability time to decrease of tensile strength to 50 %	thermal stability time to decrease of tensile strength to 50 %
30 Nylon 4.6	> 7 weeks	> 5 weeks
Nylon 6.6	about 5 weeks	about 2½ weeks
Nylon 6	about 4 weeks	about 2½ weeks

Example 2

Stress crack resistance of injection moulded testbars in zinc chloride environment.

The stress crack resistance in zinc chloride environment of nylon 4.6 was compared to that of nylon 6 and nylon 6.6 using test bars of 120 mm length, 12,7 mm width and 1,6 mm thickness. The test-bars were injection moulded from the same materials as used in example 1. The testbars were first conditioned to an equilibrium humidity corresponding to 50 % relative humidity at 23 °C and subsequently aged in a 50 weight % solution of zinc chloride in water, under a constant loading of 3 N/mm². The time to fracturing of the testbars was determined. The results of this experiment are represented in table 2.

Table 2

Fracture times of test bars under 3 N/mm ² in a 50 wt % solution of ZnCl ₂	
Nylon 4.6	> 240 hours
Nylon 6	about 10 minutes
Nylon 6.6	about 15 minutes

Example 3

Stress crack resistance of injection moulded testbars in methanol environment.

The stress crack resistance in methanol of nylon 4.6 was compared to that of nylon 6 and nylon 6.6. with test bars as used for example 2.

The testbars were first dried at a temperature of 23 °C and then provided with a side notch of 1,5 mm (1 mm of Izod-notch and 0,5 mm of razor blade notch). The testbars were subsequently aged in methanol under a constant loading of 24 N/mm². The time to fracturing was determined. The results of this experiment are represented in table 3.

Table 3Fracture times of test bars under 24 N/mm² in methanol

	nylon 4,6	> 40 hours
	nylon 6	about 15 hours
5	nylon 6.6	about 5 hours

CLAIMS

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1. Polyamide article destined for a device comprising a fuel engine, characterized in that the polyamide is a polymer of tetramethylene diamine and adipic acid or a copolymer thereof with other amide and/or ester forming compounds.
- 5 2. Article according to claim 1 characterized in that the polyamide has a relative viscosity value, as measured at 20 °C on a solution in 96 % sulfuric acid containing 1 g of polyamide in 100 ml of solution, of at least 2.
3. Article according to any one of claims 1 and 2, characterized in
10 that it is destined to be subjected to increased temperature.
4. Article according to any one of claims 1 to 3 characterized in that it is destined to be subjected to stress.
5. Article according to any one of claims 1 to 4 characterized in that it is destined to be subjected to zinc an/or chloride ion
15 containing environments.
6. Article according to any one of claims 1 to 5 characterized in that it is destined to be subjected to alcohol containing environments.
7. Article according any one of claims 1 to 6 characterized in that
20 it is on automotive vehicle part.
8. Article according to any one of claims 1 to 7 characterized in that the polyamide substantially consists of polytetramethylene adipamide.
9. Use of a polymer of tetramethylene diamine and adipic acid or a
25 copolymer thereof with other amide and/or ester forming compounds for making articles destined for a device comprising a fuel engine.
10. Use of a polymer in accordance with claims 9 characterized in that the polymer has a relative viscosity value, as measured at 20 °C
30 on a solution in 96 % sulfuric acid containing 1 g of polyamide in 100 ml solution of at least 2.
11. Use of a polymer in accordance with any one of claims 9, 10 characterized in what said polymer substantially consists of polytetramethylene adipamide.

12. Use of a polymer in accordance with any one of claims 9 to 11, characterized in that an article is made having the destination as stated in any one of claims 3 to 7.
13. Article and/or use of a polymer of tetramethylene diamine and adipic acid or a copolymer thereof with other amide and/or ester forming compounds, substantially as disclosed in the specification and examples.



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PARTIAL EUROPEAN SEARCH REPORT
which under Rule 45 of the European Patent Convention
shall be considered, for the purposes of subsequent
proceedings, as the European search report

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DOCUMENTS CONSIDERED TO BE RELEVANT			EP 82 20 1432
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X,Y	EP - A - 0 038 582 (STAMICARBON) * the whole document, in particular page 3; lines 1-3 *	1-13	C 08 G 69/26
Y	CHEMICAL ABSTRACTS, vol.67, 1967, page 3177, abstract no.33373k COLUMBUS OHIO (US) & Tech. Pap., Reg. Tech. Conf., Soc. Plast. Eng., Newark Sect., 1967 (Feb.), 75-82 H.P. de HAAN et al.: "Engineering with thermoplastics."	1-13	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			C 08 G 69
INCOMPLETE SEARCH			
<p>The Search Division considers that the present European patent application does not comply with the provisions of the European Patent Convention to such an extent that it is not possible to carry out a meaningful search into the state of the art on the basis of some of the claims.</p> <p>Claims searched completely: 1-13 Claims searched incompletely: Claims not searched: Reason for the limitation of the search:</p> <p>The search is incomplete because the uses of the polyamide article are not sufficiently defined to permit a search in the mechanical fields.</p>			
Place of search The Hague		Date of completion of the search 29-06-1983	Examiner LEROY
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	